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GAS-GENERATING SUBSTANCES

The invention relates to gas-generating substances, in particular for gas generators in belt tighteners and inflatable air-bags for protecting the occupants of motor vehicles against injuries.

With the gas generators currently used for inflatable air-bags, a gas charge in tablet or disc form or as granules or e.g. in noodle form is used as a combustible gas-evolving material. During burn-off, this gas charge generates the useful or compressed gas for the inflation of the air-bag. The disadvantage of the combustion of solid gas-evolving materials is the extremely high amount of slag produced during the combustion, which may make up more than 50% of the gas charge material used. Because of the slag and dust formed during the combustion, complicated filter stages are required in the gas generator in order to retain slag and dust particles. Otherwise the air-bag would be damaged during the discharge of these particles and the occupants may be exposed to danger.

As an alternative to these gas charges, generators containing compressed gases or air exist. Very high charging pressures are required for the formation of a sufficient gas volume, since cooling takes place during the outflow of the gases and no increase in volume is achieved through exothermic reactions as in the case of solid mixtures. In order to offset the cooling, a solid propellant fuel is frequently used, which ensures the operation of the gas generator merely through the heat of reaction during its burn-off and the additional gas evolution.

The invention is based on the object of providing a

gas-evolving material for a gas generator, in particular for a belt tightener for an inflatable air-bag for protecting the occupant of a motor vehicle against injuries, where slag retention equipment is not
5 required for the gas-evolving material.

The achievement of the aforementioned object consists in a mixture of laughing gas as oxidising agent and one or more fuels that are solid under the usual conditions
10 (room temperature and standard pressure). Used as a gas-evolving material is laughing gas (N_2O) as oxidising agent in combination with solid fuels or mixtures which react after ignition in a controlled manner in the combustion chamber to form slag-free or largely slag-free
15 free gaseous reaction products. The pressurised laughing gas is ignited together with the solid fuels by an ignition device containing an ignition charge. Use may be made as an ignition charge, for example, of an exploding wire or an ignition bridge, optionally
20 with reinforcement with a booster charge, to produce a particle-rich, hot flame.

The ignition fumes and hot combustion gases ignite the gas/solid mixture. The latter burns in the combustion
25 chamber without solid particles remaining. Filter stages that are positioned before at least one outlet opening of the gas generator housing wall may therefore be dispensed with when the gas/solid mixture according to the invention is used. If filter stages are
30 provided, the latter serve exclusively cooling purposes. The cooling may also be carried out in another manner, however, by, for example, fitting downstream of the combustion chamber a distribution compartment of the housing, from which the combustion
35 gases pass to the outside via at least one outlet opening.

According to the invention gases or gas mixtures with low intake pressure are proposed, which, as a result of exothermic conditions, produce a manifold increase in volume on burn-off and require no filters of any kind.

5 The gas or gas mixture usable according to the invention consists of the oxidising agent. In order to avoid high intake pressures, oxygen or air is dispensed with as oxidising agent. In dinitrogen monoxide (laughing gas) there exists a gas which may be easily
10 liquefied (critical pressure: 72.7 bar, critical temperature: 36.4 °C). The oxidising capacity is twice as high as that of air and in contrast to pure oxygen or air, laughing gas behaves up to at least 200 °C as an inert gas, as a result of which quiescent oxidising
15 processes are prevented even during storage at high temperature. Nitrogen monoxide (NO/N₂O, critical pressure 64 bar, critical temperature - 93 °C) may also be used in a mixture with laughing gas or as a gaseous oxidising agent on its own. In order to control the
20 reactivity of the gases, inert gases (carbon dioxide, air, helium, neon, argon) may be added. The use of nitrogen monoxide has the advantage that there is no formation of condensed portions which first have to evaporate during the burn-off reaction. Additions of
25 smell-intensive gases such as e.g. mercaptans in small amounts may make a rapid detection of leaks possible. The addition of e.g. vanillin improves the smell properties of the burn-off fumes in the application case.

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According to the invention, used as fuels are polymers from the group of the hydrocarbons, such as ethylene, propylene, isoprene, styrene, as well as those which may also contain oxygen and are derived from e.g.
35 carboxylic acids such as polyvinyl acetates, polymethacrylates, polyterephthalates and other

polyesters, polyethers, polycarbonates, and also polyoxymethylene, oligo- and polysaccharides such as sugar, cellulose, starch, polyvinyl acetals or polyvinyl alcohols. In addition, however, further
5 polymers of different compositions are also usable, provided the reaction products do not contain any dangerous components in an inadmissible amount, such as e.g. HCl, HCN, HF or phosgene. Explosive substances may also be used as additional reactive components of the
10 fuels. Examples are nitroguanidine (NiGu), derivatives of tetrazole such as 5-aminotetrazole, 5-aminotetrazole nitrate, bistetrazole amine or bistetrazole, aminoguanidine nitrate, diaminoguanidine nitrate, triaminoguanidine nitrate, guanidine nitrate,
15 dicyanodiamidine nitrate, diaminoguanidine azotetrazolate, nitrotriazolone, dicanediamidine nitrate, hexogen, octogen. The following may be used, for example, as further fuels: urea, organic acids (e.g. fumaric acid, ascorbic acid, oxalic acid), cork,
20 wood, metals (e.g. aluminium, titanium) and non-metals (e.g. boron, silicon), nitrides, azides or inorganic benzene (B_3N_3). The fuels may be applied in the form of powder, granules, pressings such as e.g. tablets, or in the case of polymers e.g. also as cut fibres or twisted
25 fibres, mats, woven fabrics, porous foams e.g. of polyurethanes. To control the burn-off, the specific embodiments may be surface-treated by being impregnated or mixed with liquids or pasty substances (inhibitors).

30 Further additives catalysts may be used, for example ferrocene and derivatives, iron or copper acetylacetonate and/or oxidising agents such as, for example, nitrates of alkali and alkaline earth elements, perchlorates of alkali and alkaline earth
35 elements, ammonium nitrate, ammonium perchlorate, zinc peroxide, perborates, peroxodisulphates, permanganates,

tin dioxide, manganese dioxide, oxidising agents
derived from the nitramines and mixtures of these
components and/or porosity generators, such as for
example ammonium hydrogencarbonate, acetone
5 dicarboxylic acid, azoisobutyronitrile and/or hollow
plastics spheres.

The ratio by weight of the fuels to dinitrogen monoxide
is preferably adjusted in such a way that a non-
10 combustible gas mixture is obtained after the reaction.
Accordingly the ratio by weight of the fuels to
dinitrogen monoxide should be adapted to the
stoichiometric proportions of a (where possible)
complete combustion. Dinitrogen monoxide is therefore
15 used to advantage in a slight excess, referred to the
fuel. The reaction products then consist substantially
of gaseous substances (CO_2 , H_2O and N_2). The gas/solid
systems described according to the invention produce,
according to how they are chosen, residue-free, almost
20 CO - and NO_x -free, reaction products, with the burn-off
property being controllable according to the nature,
proportion by weight, geometry and configuration of the
fuel.

25 The invention will be described in detail below through
examples, without however limiting it:

Examples:

30 All the tests are carried out in a sealed pressure
vessel with a volume of approx. 120 ml. The ignition
is performed electrically with 150 mg of a
boron/potassium nitrate mixture as booster. The
laughing gas is fed into the vessel by means of a
35 compressor. The weighed portion of laughing gas may be
determined by weighing of the vessel before and after

the charging. The internal pressure in the vessel comes after the feeding to approx. 4 Mpa. The solid selected is weighed into the vessel prior to the charging with laughing gas. The pressure measurement is carried out
5 in the vessel by piezoelectric pressure elements. Maximum pressure (p_{max}), pressure increase time (Δt) and time until maximum pressure ($t_{p_{max}}$) is reached are measured. In Example 1 the behaviour of the laughing gas without additional fuel is shown (see Table 1).
10 Heating and pressure increase takes place in the vessel due to the ignition, which pressure increase however differs significantly from the burn-off behaviour in the presence of solids, as Examples 2 - 4 show. In Examples 2 - 4 the burn-off behaviour of
15 various materials such as polystyrene, nitroguanidine and starch is represented. A summary of the results is given in Table 1.

Table 1: Summary of results of Examples 1 - 4

Example	Solid	Weighed portion solid [g]	Weighed portion laughing gas [g]	p_{max} [Mpa]	Δt [ms]	t_{Dmax} [Mpa]
1	-	-	11	42	11.2	15.4
2	P o l y - styrene	1.1	11	62	2.2	7.1
3	Nitroguani dine	1.1	11	69	1.1	4.4
4	Starch (flour)	1.1	11	64	4.2	11.5

In Examples 5 - 9 the influence of various make-ups and geometries of the solid on the burn-off characteristics in the pressure vessel is shown. Two solids are used, first of all starch in various modifications, here characterised by the particle diameter, and secondly nitroguanidine as a loose powder with a grain size of approx. 50 μm and as tablet with a diameter of 7 mm and a depth of approx. 2.3 mm. A summary of results is given in Table 2.

Table 2: Summary of results of Examples 5 - 9

Example	Solid	Geometry	p_{\max} [Mpa]	Δt [ms]	t_{\max} [Mpa]
5	Starch	Sphere D: 1 - 2 μm	63.7	4.2	11.6
6	Starch	Sphere D: approx. 250 μm	66.4	7.01	21.9
7	Starch	Sphere D: approx. 1 mm	61.7	9.4	29.9
8	Nitroguani- dine	P o w d e r grain size approx. 50 μm	68.6	1.1	4.4
9	Nitroguani- dine	Tablet D 7 mm, D 2.3 mm	60.1	10.7	38.5

Very good estimates of gas composition and combustion temperatures are obtained by means of thermodynamic calculations. In Examples 10 - 12 a thermodynamic calculation is carried out with the ICT code for polystyrene, nitroguanidine and starch. It is based in each case on a solid-lauging gas mixture of 9 to 91 wt %. A summary of the results is given in Table 3.

Table 3: Summary of results of Examples 10 - 12

Example	Combustion temperature [K]	N ₂ [vol. %]	CO ₂ [vol. %]	H ₂ O [vol. %]	O ₂ [vol. %]	CO [vol. %]	NO _x [vol. %]
10	4075	63.1	21.2	10.4	5.2	< 0.001	0.06
11	2710	64.9	2.4	5.0	27.5	< 0.001	0.14
12	3181	61.2	9.8	8.2	20.6	< 0.001	0.11